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PREPARING LOW-ENERGY SURFACES FOR BONDING.(U)
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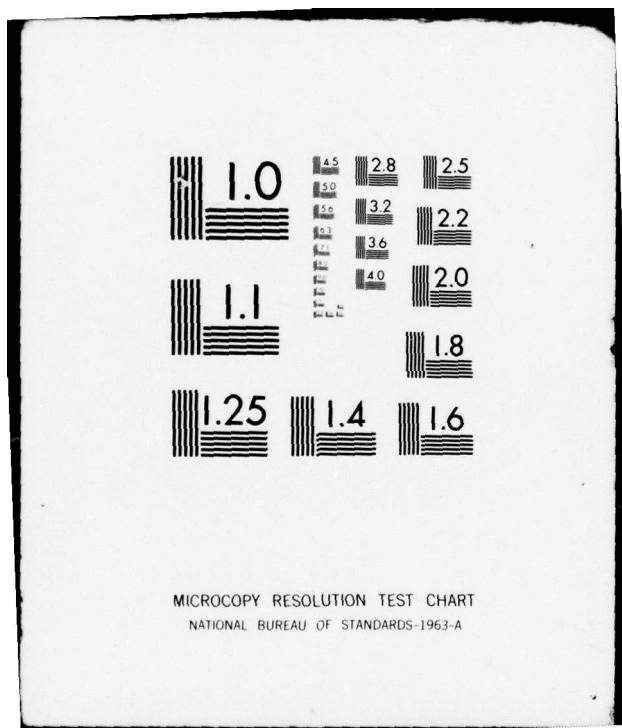
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Technical Report 30

Preparing Low-Energy Surfaces for Bonding

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January 1978

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PROPELLANTS, EXPLOSIVES AND ROCKET MOTOR ESTABLISHMENT

WALTHAM ABBEY, ESSEX

Technical Report No 30

Approved 13 June 1977

PREPARING LOW-ENERGY SURFACES FOR BONDING

by

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SUMMARY

Techniques for preparing low-energy surfaces prior
to adhesive bonding are reviewed, and the mechanisms
whereby the various treatments work are discussed in
detail.

CONTENTS

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1 INTRODUCTION

Over the years very many empirical surface treatments have been developed both for metals and non-metals, all improving the subsequent bondability of the substrate by organic adhesives. Various reviews[1-5] give details. It is not our purpose to list again those methods which are particularly applicable to low-energy surfaces. Indeed there have been relatively few additional developments recently. However considerable advances have been made in understanding the mechanisms whereby the various treatments work. A survey of this elucidation of the scientific principles involved is preceded by a brief introductory summary of the main concepts such as surface energetics, wettability, and surface chemistry; together with the techniques used in studying them, such as the measurement of contact angles, and the powerful techniques of Auger and X-ray photoelectron spectroscopy, used for analysis of the surface. Then after a brief description of the main types of surface treatment in ascending order of complexity, particular groups of low-energy materials are considered in turn. Finally, irradiation techniques are reviewed.

1.1 Surface Energy

The surfaces of rubbers and plastics have low surface energies (generally less than 50 mJ/m^2), as distinct from those of metals, with energies of the order of 1000 mJ/m^2. An energetic surface will make the liquid spread on it, while a surface of low-energy will let it remain as a discrete drop. So sufficient surface energy is needed to cause spreading of the adhesive and thus intimate molecular contact between it and the substrate: without that it is clearly impossible to achieve a bond. Poor wetting may be due to contamination, which may be removed by solvent cleaning, or it may be due to the molecular structure of the surface, which may be modified by chemical treatment.

The experimental approach to surface energetics is primarily by observing contact angles between liquids of various surface tensions and the substrate in question. Zisman[6] and co-workers made the first approach to the characterisation of low-energy surfaces: they found an empirical rectilinear relation between the cosines of the contact angles found on a given surface

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with a series of saturated hydrocarbon liquids, and their surface tensions. They defined a critical surface tension of wetting as the extrapolated value of surface tension corresponding to complete wetting (cosine = unity; zero contact angle). Even if a non-homologous series of liquids were used, the points fell close to a straight line which extrapolated to the critical surface tension, the highest at which a liquid would just spread and give a zero contact angle. This value characterises the wettability of the low-energy surface.

Levine, Ilkka and Weiss[7] found a linear relationship between the critical surface tensions of a series of polymers and the strength of joints between the polymers and an epoxy adhesive, thus emphasising the fundamental importance of wetting in the formation of an adhesive joint. Fowkes[8] introduced the idea of the additivity of intermolecular forces, ie that the surface energy of a solid (γ_S) consists of contributions from dispersion (γ_S^D) and polar (γ_S^P) forces, and that the geometrical mean of the dispersion force components $(\gamma_S^D \gamma_L^D)^{\frac{1}{2}}$ across an interface (where γ_L^D refers to the wetting liquid) is a reliable measure of the interaction energy caused by dispersion forces. Owens and Wendt[9] and Kaelble and Uy[10] extended this to include the polar interaction, and established that dispersion and polar forces each only interact across interfaces with their like. Kaelble[11] thus evaluated the dispersion and polar contributions to the surface energy of a number of solids. He defined[12] a wettability envelope for a given substrate, by graphically plotting the contribution of the dispersion forces against that for the polar ones. If the characteristic of any adhesive (γ_L^P, γ_L^D) falls outside the curve, good wetting and hence a good joint will not occur. However, if a surface pretreatment can somehow increase the total surface energy so that the envelope is extended to include the adhesive's characteristic, then good wetting will take place. Many methods of increasing the surface free energy are discussed in later sections: the scientific principles underlying them are becoming well established.

Baszkin and Ter Minassian-Saraga[13] have quantitatively determined the surface densities of the polar sites of polyethylene as the surface is oxidised. They show that as the temperature is raised to about $85^\circ C$ there is a decrease in wettability, due to the increase of chain mobility leading to

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the redistribution of external polar groups into the bulk. Owens[14] has shown that corona-treated polyethylene bonded after heating gives bond strengths which are considerably reduced by raising the heating temperature from 60 to $80^{\circ}C$, presumably for the same reason. He attributes the bond to hydrogen bonds (from enolised keto groups formed by the corona treatment) with carbonyl groups. He also has demonstrated[15] in the case of poly(ethylene terephthalate) that molecular motion causes the loss of bondability, which is based on hydrogen bonds between phenol groups created by corona or UV irradiation and carbonyl groups in the other surface.

The basic principles underlying the need to prepare low-energy surfaces for bonding also apply to high-energy surfaces, although the emphasis is different. As indicated above, it is helpful to increase the surface energy of low-energy plastics and rubbers. Paradoxically, this is also necessary for intrinsically high-energy materials, because the original unstable high surface energy has normally been masked by the acquisition of contaminants, which must be removed before bonding. Even in the case of noble metals, such cleaning is not necessarily simple. A remnant aqueous monolayer will greatly reduce the spreading of liquid water.[16,17,18] There is also spectroscopic evidence of persistent contamination by air-borne hydrocarbons.[19]

Even if good wetting is achieved, a strong bond does not necessarily follow. If there is a weak boundary layer on the adherend,[20] the joint will of course be no stronger than the layer.

1.2 Surface Analysis

The direct examination of surfaces and contaminants on them has recently become possible by the use of Auger electron and X-ray photoelectron spectroscopy (AES and XPS, respectively). These two techniques are extremely useful in adhesion studies in that both enable the composition of the outer 1 to 5 atomic layers of the surface of a solid to be analysed. The basic technique in AES consists of bombardment of the surface with a beam of electrons in the range of 1 - 5 keV and analysis of the energies of the ejected electrons, which usually provides only an elemental analysis. In XPS, photoelectrons (and Auger electrons) are generated when the surface is flooded with soft X-rays; the photoelectrons have discrete binding energies whose values depend upon both the

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element and its state in the atomic matrix in the surface. Therefore, it is possible to determine both the concentration and chemical state in the surface. The two techniques are in many ways complementary. AES gives good spatial resolution since a narrow (1 - 50 μm) electron beam is used, while with XPS such spatial resolution cannot as yet be obtained, since it depends on X-ray photons to excite photoelectrons. The advantage of XPS is, however, that charging effects are minimised and surfaces of insulators can be more easily analysed.

1.3 Surface Treatment

As indicated above, surface preparation for bonding can be of many different types, depending on the mechanism of amelioration intended. The theories of adhesion and adhesive action have been recently reviewed,[21] and it is clear that adhesion is no simple phenomenon. Thus we will consider the purpose of surface treatments in the light of the theories, starting with the simplest. Probably the first and main purpose is to clean the surface by removing contaminants. The simplest way to remove grease, etc is with an organic solvent, either by wiping with a damped cloth or by liquid or vapour degreasing.

Next is abrasion, either with abrasive paper or wire-brush, or by grit-blasting. This not only removes surface contamination, it removes the surface and perhaps a weak boundary layer as well. It also increases the apparent surface energy. It is often thought that a roughened surface is preferable, as it enables 'keying' of the adhesive into the surface, and there is evidence for this mechanism with fibrous adherends such as textiles, leather and wood. There is evidence also[22] that the mechanism of adhesion to porous anodic films on aluminium involves keying of the polymer into the pores. Surface rugosity also can affect the kinetics of wetting by the adhesive[23,24] and it has been shown[25] that the rate of spreading on a very rough surface is much greater than on a polished surface. However, in practice adhesives are forcibly spread on to substrate surfaces and this driven flow causes the adhesive to outrun any surface capillary spreading phenomenon.[24] It has also been shown[26,27] that random roughness, as distinct from the more uniform surface (of aluminium alloy) achieved by polishing, can increase the strength of a joint, probably by changing the stress distribution at the interface.

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However abrasion is usually insufficient as a treatment for low-energy surfaces, and chemical treatment is often needed to increase the surface energy. Specific chemical treatments will be discussed below, for each substrate material in turn.

2 FLUOROCARBON POLYMERS

The fluorocarbon family includes polytetrafluoroethylene (ptfe), poly-chlorotrifluoroethylene (pctfe), fluorinated ethylene-propylene copolymer (fep), polyvinyl fluoride and polyvinylidene fluoride. They all possess very low surface free energies, about 30 mJ/m^2 or less, and are extremely inert polymers. The most common surface treatment is etching, ie eating away the surface with an aggressive or mordant reagent.

2.1 Etching Treatments

The treatment for fluorocarbon polymers is usually based upon metallic sodium dissolved in a solution of naphthalene in tetrahydrofuran. Proprietary solutions are available and it is also possible to purchase ptfe already treated by such chemical processes.

This sodium naphthalene treatment requires immersion of the polymer in the fresh treating solution at room temperature, then rinsing in water, then in acetone, followed by thorough washing in water again and finally drying. The etching process produces a dull brown colour on the fluorocarbon's surface and this colouration intensifies as the etching time is increased. It has been suggested[28] that this colour change may provide a useful quality control check for procurement of uniformly and reproducibly etched material.

Nelson, Kilduff and Benderly[29] have shown that the etching solution attacks only the surface regions of the fluorocarbon polymer. They examined a cut section of etched ptfe and from optical microscopy determined that the depth of the coloured surface region was about one micrometer. However they reported that the bulk electrical properties of the treated and untreated polymer were virtually identical and that their electron diffraction patterns were indistinguishable. They attributed these observations to the thinness of the treated surface layer or to the treated material having the same structure as the bulk material. Benderly[30] has since reported that the treated

material does have a substantially lower surface resistivity than the untreated material, so confirming the former explanation. Purvis and Beck[31] have ascribed the brown colouration to a carbonaceous surface being formed as a result of the extraction of fluorine atoms by the etching solution. Their detection of fluoride ions in the expended etching solution provided some evidence for this proposed mechanism. Further support has recently come from the work of Miller et al[32] and Andrews and Kinloch.[33] These latter authors used infrared attenuated total reflectance (atr) spectroscopy to examine the surface regions or untreated and etched fluorinated ethylene-propylene copolymer. The spectra were identical and no absorption bonds were observed at the frequencies appropriate to hydrocarbon or fluorocarbon unsaturated groups. Now Polchlopek[34] has reported that a continuous depth of about 1 μm of the material to be identified is required for detection by the type of atr spectroscopy employed in the above investigation. Therefore, since 1 μm was the etch depth determined by Nelson et al,[29] further characterisation of the fep surfaces was conducted by placing samples of the fluorocarbon in a 1 mass % solution of osmium tetroxide for six days. Osmium tetroxide reacts with carbon-carbon double bonds to produce a dark appearance. In the case of the untreated material no visible colour change occurred after immersion. However the surface of the etched fep was considerably darkened; by sectioning perpendicular to the surface and examination in the optical microscope the depth of the darkened surface layer was found to be about 1 μm, in good agreement with the above comments. It is the presence of these conjugated carbon-carbon double bonds in the surface regions that are responsible for the brown colouration. XPS studies[35] have confirmed that unsaturation is introduced by the etching treatment and have shown that $\supset C = O$ and -COOH groups are also introduced.

Several workers[12,36,37] have reported a large increase in surface free energy obtained by etching fluorocarbon polymers in sodium naphthalene and this is convincingly demonstrated by the wettability envelopes[12] of untreated and etched ptfe shown in Figure 1. It is undoubtedly the increase in wettability which is usually responsible for the increased adhesion to etched surfaces.

The effect of a proprietary sodium naphthalene etching treatment on the strength of tensile butt joints is given in Table 1. The adhesive was an epoxy-polyamide and the beneficial effects of the etching treatment are obvious.

TABLE 1

Effect of Various Surface Pretreatments on the
Bondability of ptfe and pctfe[38]

Fluorocarbon	Butt joint strength (MPa) for given treatment			
	No surface treatment	Abraded	Etched	Abraded and etched
ptfe	Fell apart	Fell apart	10.8	13.2
pctfe	2.6	7.7	19.4	20.7

Similar increases in peel strength are recorded when ptfe is bonded to itself with a neoprene rubber adhesive, as shown in Figure 2. As may be seen an optimum etching time of about 15 - 30 s is indicated.

The effect of etching time is also shown in Figure 3 for model adhesive joints consisting of a crosslinked styrene-butadiene rubber bonded to a fluorinated ethylene-propylene copolymer.[37,39] These results enable the mechanisms of adhesion to be identified since the value of the "intrinsic adhesive failure energy", P_o, depends solely upon the physical and chemical nature of the adhesive/substrate interface and, if only secondary forces are acting, equals the thermodynamic work of adhesion, W_A. For the rubber/unetched-fep interface the value of W_A is about 50 mJ/m^2 and for the rubber/etched-fep interfaces about 70 mJ/m^2. Now in the case of the former interface P_o is approximately equal to W_A but for the etched substrates $P_o \gg W_A$. This arises because the etching treatment not only increases the surface free energy of the fep but also introduces a significant concentration of carbon-carbon double bonds into the etched substrate's surface regions. Therefore, since dicumyl peroxide in the compounded rubber will initiate reactions

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between the rubber molecules and unsaturated groups in the substrate surface, primary covalent bonding will be established across the rubber/etched-fep interface during curing of the elastomer. The observed increase of P_o over and above W_A for these interfaces is thus to be expected since the calculation of W_A takes into account only secondary force interactions (eg van de Waals forces). As etching proceeds, however, the fep surface layer suffers degradation and this is reflected by the locus of joint failure progressively occurring via fracture of the substrate surface regions. Thus the two effects of etching, namely (i) increasing the concentration of carbon-carbon unsaturation (and hence the likelihood of interfacial covalent rather than secondary bonds) and (ii) reducing the strength of the etched regions, result in an optimum etching time for maximum joint strength.

Finally, as might be expected, the unsaturated and oxidised etched layer is more reactive, not only to the adhesive but also to ultraviolet radiation, and there are several references to the instability of the adhesive bond between sodium-etched fluorocarbon polymers and other materials in the presence of UV light.[28,30,40] The effect of accelerated ageing tests on etched ptfe joints bonded with a polyurethane adhesive and exposed to UV light is given in Table 2.

TABLE 2

Peel Strength of Etched ptfe Joints Aged in a Weather-Ometer[28]

Substrate	Peel strength (kN/m) after ageing			
	0 h	100 h	200 h	500 h
Etched ptfe	2.00	0.79	0.35	0.00
Etched ptfe : UV absorbers	2.00	-	-	1.21

The failure site of the aged joints was between the etched ptfe surface layer and unetched ptfe bulk material. Also shown are the results from incorporating uv absorbers, such as carbon black, in the ptfe film and hydro-

quinone into the adhesive, which considerably increases the durability of the joints upon exposure to UV radiation.

Applications in which proprietary sodium naphthalene treatments have played an important role include: bonding of ptfe bushes to metal, bonding ptfe insulation to electrical components, preparing seals to ptfe and ptfe insulated connectors, preparing seals between polyethylene and ptfe insulated wire and connector terminals, and improving potting seals.

2.2 Abrasion

Abrasion is usually a very poor surface treatment for fluorocarbon polymers, as may be seen from the results in Table 1. However, Lerchenthal and co-workers[41,42,43] have claimed that abrading substrates beneath reactive adhesives may dramatically increase joint strengths compared to normal abrasion methods in air. Results for ptfe bonded to itself and to aluminium with an epoxy-polyamide adhesive are shown in Table 3.

TABLE 3

Abrasion Surface Treatments for ptfe

Joint	Treatment of ptfe			
	Abraded in air		Abraded beneath epoxy/vinyl acetate mixture	
	Tensile shear strength (MPa)	Locus joint failure	Tensile shear strength (MPa)	Locus joint failure
ptfe - aluminium	0.98	Interfacial	5.71	Interfacial
ptfe - ptfe	0.98	Interfacial	6.67	Interfacial

Whether the abrasion beneath an epoxy/vinyl-acetate mixture arises from better wetting or from reaction of the mixture with free radicals generated in the polymer surface by the abrading has yet to be firmly established.

2.3 Morphological Changes

Schonhorn and Ryan[44] have reported that heterogeneous nucleation and crystallisation of fep melt against high-energy surfaces (eg gold, aluminium)

produces a transcrystalline surface on the fluorocarbon of high mechanical strength and increased surface free energy. Indeed the critical surface tension may rise from 18.8 to 40.4 mJ/m^2.[45] Other workers[35] have suggested that this is due to the formation of a thin layer of oxygen-containing hydrocarbon material rather than highly crystalline fep. A surface is produced which is amenable to conventional bonding. The tensile shear strengths of aluminium/epoxy/fep joints where the fep has been subjected to this and other surface treatments is shown in Table 4. Schonhorn and Ryan concluded that gold films deposited electrochemically are not effective, perhaps because they are contaminated or complexed with a variety of organic compounds, (eg cyanide, citrate) normally used in plating baths.

TABLE 4

Various Surface Treatments for fep

Surface treatment of fep	Tensile shear strength (MPa)
None	0.69
Nucleated and crystallised against electrochemically deposited gold	4.82
Nucleated and crystallised against evaporated aluminium	12.41
Nucleated and crystallised against evaporated gold	19.30
Etched in sodium naphthalene solution for 40 s	20.00

Evaporated films of gold are far more effective in generating a transcrystalline region of high strength and surface free energy. Further, gold is also more effective than aluminium oxide in this respect. The basic difference may be in the density of nucleating sites on the surface. If there are too few, ordered transcrystalline growth may not take place.

2.4 Aluminium/Alkali Treatment

Roberts and co-workers[46] have recently described a new method for bonding gold to fluorinated-ethylene-propylene copolymer which yields high joint

strength without affecting the electrical properties of the virgin polymer surface. The method consists of depositing a 100 nm aluminium layer on the film by evaporation, removing it by washing the sample in dilute sodium hydroxide, followed by deposition of gold by evaporation. X-ray photo-electron spectroscopy (XPS) indicated significant chemical modification of the film's surface, apparently consisting of the generation of a thin and perhaps continuous surface layer of oxygen-containing hydrocarbon material, as a result of the aluminium deposition. In contrast scanning electron microscopy indicated the surface topography was relatively unaffected. It therefore appeared that the increased joint strength could be attributed to the increased surface free energy of the fluorocarbon.

3   POLYOLEFINS

Like the fluorocarbon polymers discussed above, polyolefins such as low- and high-density polyethylene, polypropylene and poly(4-methyl pentene-1) cannot usually be bonded to give reproducible high strengths unless some form of surface pretreatment is employed. Many treatments have been reported to improve the adhesion to polyolefin surfaces; these include corona[47,48,49] and glow discharge,[50,51,52,53] chemical attack with chromic acid,[54,55,56] with sulphuric acid[2] or with peroxydisulphate,[57,58] fluorination,[59] solvent etching,[60] exposure to flame and hot-air blasts[61] and melt crystallisation against high-energy surfaces.[62,63] The aims of all these varied surface treatments are to remove any contamination or weak boundary layer on the polyolefin's surface, increase the surface free energy of the material and make the surface more receptive to bonding.

3.1 Solvent Cleaning

The simplest treatment is solvent etching,[60] and the effect of dipping a polypropylene substrate into a trichloroethylene solvent vapour prior to bonding to aluminium using an epoxide adhesive is shown in Figure 4. The effect of a short exposure time on the joint strength is spectacular but over-treatment may readily occur causing a rapid decline in joint strength. The trichloroethylene vapour imparted a dull white finish to the smooth polymer surface, and from scanning electron microscopy studies the authors concluded that the untreated polymer possessed a weak surface layer which

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was removed by the solvent treatment. This treatment also resulted in a highly porous surface (possibly caused by the solvent attacking the amorphous regions of the surface preferentially). This mechanism for the improvement in joint strength was indirectly supported by the solvent-treated surfaces having a wettability inferior to that of the untreated polymer, as indicated by the contact angle data shown in Table 5.

TABLE 5
Wettability of Untreated and
Solvent-Cleaned Polypropylene

Pretreatment	Contact angle of	
	Water	Epoxide adhesive
None	90°	26°
Solvent-vapour	98°	34°

The decline in joint strength for etching times longer than about ten seconds is probably due to degradation and weakening of the surface layer.

3.2 Chemical Etching

One of the most common surface treatments for polyolefins is etching in chromic acid and a detailed study of this method has recently been reported by Blais et al.[54] They employed chromic acid solutions to etch linear (high-density) and branched (low-density) polyethylene and isotactic polypropylene. Apart from measuring joint strengths they also characterised the etched surfaces by atr infra-red spectroscopy, contact angle measurements and electron microscopy.

Spectroscopic examination revealed extensive chemical changes only in the case of low-density polyethylene, with an increasing concentration of $-OH$, $>C = O$ and possibly $-S (= O)_2 OH$ groups in the surface layer. However, as pointed out previously, atr spectroscopy is not a true surface technique and has a relatively large sampling depth compared to the likely etch depth. This is why new surface analytical techniques such as Auger and X-ray photoelectron

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spectroscopy (XPS) have recently been used to study chemical changes arising from surface pretreatments[64,65] and to identify accurately the locus of failure in adhesive joints.[19,66] Employing XPS analysis Briggs and co-workers[64] detected the presence of $- OH$, $>C = O$, $- COOH$ and $- S (= O)_2 OH$ groups in the outermost surface regions of both chromic-acid etched poly-ethylene and polypropylene. Further, they showed that the essential difference between etching polypropylene for one minute at $20^{\circ}C$ or six hours at $70^{\circ}C$ was in the depth of attack achieved rather than any increase in the degree of surface oxidation. In the case of polyethylene, however, both the etching depth and degree of surface oxidation increased with etching time. Nevertheless, for both polyolefins considerable improvement in joint strengths were recorded after etching for only one minute at $20^{\circ}C$ but increased etching times did not lead to increased joint strengths, possibly due to the limiting strength of the polyolefin substrate.

Blais et al have also studied the effect of etching time. They realised that the enhancement of bonding by a treatment would eventually lead to the situation where joint failure occurs by cohesive fracture of the polyolefin substrate, as observed by Briggs and co-workers. Since measurements under these conditions obviously do not reflect the effectiveness of the surface treatment they therefore used (i) an adhesive which would give an extremely low bond strength to an untreated polyolefin surface, (ii) an adhesive with reasonable cohesive strength and (iii) a joint geometry sensitive to varia-tions in interfacial adhesion. They chose a polyacrylic acid adhesive, plasticised with a little ethylene glycol, and a modified 90° peel test geometry. The peel strength is shown as a function of etching time in Figure 5. The polypropylene shows an approximately 170-fold increase in peel strength after a 100 second etch but little improvement for a more prolonged attack, while both polyethylenes exhibit a rapid increase in joint strength with longer etch times.

The work of both Blais et al and Briggs et al indicated that there was little correlation between the contact angles of water on the etched surface and resulting joint strength. However, Shields[2] has shown that chromic acid etching produces a very rough surface and it is well established[67,68] that

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surface roughness alone may result in contact angle changes. Scanning electron micrographs obtained by Shields are shown in Figures 6 (a-d) and it may be seen that the surface of untreated polypropylene was smooth but marred by the presence of small pits of less than 1 µm in diameter. Changes in the surface topography were insignificant for etching periods of up to ten minutes in cold chromic acid. However, after a twenty-minute cold etch the population of pits had increased and hole diameters enlarged to about 8 µm, though considerable areas of smooth surface remained. Hot chromic acid etching had a more pronounced effect on the surface; the whole surface was of a rugose nature and contained craters with diameters approaching 10 µm. Blais et al found far less increase in the surface roughness of polypropylene upon chromic acid etching but did record interesting observations for a polypropylene sheet which had been initially annealed to produce large spherulitic, crystalline structures. Before etching the sample was quite featureless yet the spherulitic areas became visible after etching, indicating that the less ordered, amorphous material between the spherulites' arms and boundaries were more rapidly attacked than the highly crystalline arms themselves. This observation substantiates some earlier conclusions reached by Garnish and Haskins[60] who found that different grades of the same polymer showed different susceptibilities to pretreatments and suggested that this was linked to the size of the crystalline spherulites in the material. Obviously different polyolefins may exhibit even more marked effects and this adds another degree of complexity to surface pretreatment considerations.

With the chemical and physical changes induced by chromic acid etching elucidated, it might be hoped that a unified mechanism for the improvement in adhesion would be identified. Shields concluded that the effectiveness of chromic acid treatments was mainly due to their ability to produce a roughened surface which increased the surface area and enabled mechanical keying of the adhesive. However, the observation of relatively smooth surfaces by Blais et al, associated with considerable increases in joint strength, suggests that this cannot be the major mechanism operating. Briggs et al ascribed the increases in adhesion to increased surface polarity and some support for this mechanism also comes from the work of Rauhut,[61] shown in Figure 7, where a correlation is proposed between increased surface polarity,

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as reflected by the critical surface tension, γ_c, and joint strength. Never-theless, Blais et al feel that, while increased surface polarity may play a minor role in the case of polyethylene, the major mechanism is the removal by the etchant of a weak boundary layer covering the polyolefin's surface; Garnish and Haskins also propose this mechanism. However, XPS examination by Briggs and co-workers of a fractured joint which had consisted of untreated polyethylene and epoxide adhesive gave no evidence of transfer of the poly-ethylene to the epoxide; this is evidence against the weak boundary layer concept. Therefore there is no single, readily identifiable mechanism and just as different polyolefins and grades of polyolefins respond differently to etching, due to molecular-weight, chemical and morphological differences, so these various mechanisms may contribute to various extents depending upon the interface involved.

Morris[57,58] has proposed the use of an aqueous ammonium peroxydisulphate solution for treating polyethylene and polypropylene; the effect of immersion time and temperature is shown in Figure 8. No differences were apparent between the atr infra-red spectra of untreated and treated samples; hence if the polymer was oxidised by the peroxydisulphate the effect was confined to the immediate surface regions. However, the critical surface tension of the treated material was 5 mJ/m^2 higher. Further, an insoluble gel fraction was present in the treated material, about 1% by weight of the original polymer, but was absent in the untreated samples. Thus, Morris concluded that treat-ment of polyethylene and polypropylene with a peroxydisulphate solution led to the formation of a surface layer of crosslinked, entangled molecules and that this increased the mechanical strength of the surface region and resulted in higher joint strengths. Again no direct evidence was presented for the presence on the original untreated polymer surfaces of a weak boundary layer, which needed strengthening.

4 NYLONS AND OTHER PLASTICS

Other plastics such as polyvinyl chloride, polyethylene terephthalate[69] polyacetals[70,71] and nylons do not present such a severe problem to the adhesive technologist as do the fluorocarbon polymer or polyolefin families. This is because they have somewhat higher surface free energies but neverthe-

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less, in order to obtain high joint strengths approaching the cohesive strength of the substrate, some form of surface pretreatment is often necessary.

This is evident from Table 6 where the effect of various surface treatments on nylon 6.6 is shown for two different adhesive types. For the epoxide adhesive solvent-cleaning and abrading is as effective as the chromic-acid etching treatments and only an acid potassium permanganate etch followed by application of a resorcinol-formaldehyde primer results in the highest joint strengths (ie when the cohesive strength of the nylon 6.6 is reached). The interface between the nylon and resorcinol-formaldehyde primer probably has intermolecular hydrogen and covalent bonds established across it and this is reflected in the high joint strengths.

Alternatively, in the case of the cyanoacrylate adhesive a chromic-acid etch, particularly at elevated temperatures, results in high joint strengths. This may possibly arise from (i) the greater penetration of the cyanoacrylate, due to its much lower viscosity, into the etch-pits on the nylon's surface and (ii) the cyanoacrylate's greater reactivity towards the more polar etched surface. These results illustrate that the total interface, ie adhesive as well as substrate, must be considered when selecting an effective surface treatment.

Abu-Isa[72] has studied the iodine treatment of nylon materials. This treatment essentially consists of dipping the nylon in an iodine-potassium iodide solution and quickly rinsing the adsorbed iodine out of the nylon surfaces using glycol-water-thiosulphate as a wash solution; this considerably increased the strength of a metal film subsequently plated onto the treated nylon surface. It was found that the strength of the plating was dependent upon the nature of the nylon surface (crystallinity, molecular weight, etc), the duration of the iodine treatment, and the nature and conditions of the wash solution. Scanning electron micrographs of the nylon surface demonstrated that only a shallow etch pattern was introduced and thus mechanical keying between the polymer and plating was not considered to be of prime importance. However, under certain circumstances the overall degree of crystallinity was decreased and the type of crystalline structure present changed. Further, the polymer was softened, low molecular-weight fractions and monomers extracted

and the level of surface polarity raised. These last changes were considered to be responsible for the enhancement of adhesion to the treated nylon material.

TABLE 6

Effect of Surface Treatment on Tensile Shear Strength
of Nylon 6.6 Aluminium Joints[2]

Surface treatment	Adhesive	Lap shear strength (MPa)	Locus of joint failure
Solvent cleaning	Epoxy	2.92	C
	Cyanoacrylate	3.95	I/C
Solvent cleaning + abrasion	Epoxy	3.58	I
	Cyanoacrylate	3.37	I/C
15% chromic-acid; etched for 7 min at 20°C	Epoxy	4.31	I/C
	Cyanoacrylate	4.76	I/C
50% chromic-acid; etched for 30 s at 50°C	Epoxy	3.21	I
	Cyanoacrylate	6.42	C*
50% chromic-acid; etched for 120 s at 50°C	Epoxy	2.77	I
	Cyanoacrylate	5.72	C*
Acid potassium permanganate; 5 min at 90°C	Epoxy	3.76	I/C
	Cyanoacrylate	6.45	C*
As above + resorcinol-formaldehyde primer	Epoxy	6.05	C*
	Cyanoacrylate	5.56	C*

Note: I = interfacial

C = cohesive in adhesive

C* = cohesive in nylon 6.6

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5 PLASTIC LAMINATE MATERIALS

Plastic composites such as glass- or carbon-fibre reinforced composites are being increasingly used in many diverse applications. These materials have low surface energies, will not strongly adsorb water, form oxides or corrode in moist environments. They are usually based upon epoxy or polyester resins and are, therefore, more polar than the fluorocarbons or polyolefins (see Table 8) which makes them more receptive to adhesive bonding. This combination of properties results in surface treatments being required which simply remove contaminants such as oils, mould lubricants or general dirt. There are two main techniques used to achieve this[73] (i) abrasion and solvent-cleaning and (ii) the tear-ply method.

For carbon-fibre reinforced plastics it has been reported[74] that rubbing with an abrasive cloth of roughness grade 150 and subsequently rinsing with perchloroethylene to remove abrasive dust was sufficient treatment. The abrasive treatment removed the contaminants and the resin film from the laminate surface and exposed the outer carbon fibres. Joints made with this treatment resulted in the carbon-fibre reinforced plastic, rather than the adhesive, failing. Lerchental and co-workers[43] have suggested that for glass-fibre polyester laminates higher joint strengths may be obtained if the abrasion is conducted beneath a "reactive primer". The results shown in Table 7 are for lap-shear joints consisting of glass-reinforced polyester laminates bonded with an unsaturated polyester adhesive. The improvement in joint strengths observed when the abrading was performed beneath a "reactive primer" was ascribed to the initiation of chemical bonds between substrate and adhesive via the mechanochemical creation of free radicals on the substrate surface. This is certainly more likely to occur in these examples than when bonding fluorocarbons (see Section 2) or polyolefins, but improved wetting may still play a role. An interesting feature of these results is that abrading beneath different "reactive primers" gave various joint strengths but all the joints failed by cohesive fracture in the substrate. This may arise from the adhesive/primer adjacent to the substrate having different mechanical properties (and thus giving rise to different stress concentrations in the surface of the glass-laminate substrate) depending upon the "reactive primer" employed. This would then result in a range of joint strengths being recorded

but all the joints could well fail by cohesive fracture in the surface regions of the substrate.

The second technique is the tear-ply method. In designing the laminate one ply of fabric, such as Dacron or equivalent, should be installed at the bonding surface as illustrated in Figure 9. Just prior to bonding the tear-ply is removed and a fresh, clean bondable plastic surface is exposed.

TABLE 7

Lap-Shear Strength of Glass-Fibre Polyester Laminates
Bonded with a Polyester Adhesive

Reactive primer	Abraded in air		Abraded beneath reactive primer	
	Strength (MPa)	Locus of joint failure	Strength (MPa)	Locus of joint failure
1 : 9 mixture of maleic anhydride + ethyl acetate	3.1	Interfacial	5.2	C
1 : 9 mixture of acrylonitrile + styrene	6.2	Interfacial	9.0	C
1 : 9 mixture of methyl methacrylate + styrene	6.2	Interfacial	8.8	C

Note: C indicates cohesive failure in surface regions of laminate substrate

Crane et al[75] have compared several pretreatment methods for carbon-fibre composites and their results are given in Table 8.

There is no obvious correlation between surface free energy and joint strength and the authors concluded that a tear-ply serves only to protect the composite surface from contamination between manufacture and bonding (its intended purposes, of course!). The only pretreatment studied that significantly improved bond strength over that of the untreated surface was abrasion.

TABLE 8

Effect of Pretreatment on Strength of
Epoxy/Carbon-Fibre Composite Joints

Pretreatment employed	Surface free energy (mJ/m^2)	Lap-shear strength (MPa)
None	33.3	16.5
Light sanding	43.1	20.6
Heavy sanding	58.0	20.6
Nylon tear-ply	46.8	15.3
Nomex tear-ply	68	16.0
Nitric acid treated	73.4	9.8

6   RUBBERS

Rubbers are mostly easily bonded to other materials during vulcanisation
and proprietary one-component and two-component adhesive systems for such
rubber-to-rubber and rubber-to-metal bonding are available.[76,77,78] The
uncured rubber surface should be clean and free from contaminants such as
mould-release agents and the metal substrate should be vapour-degreased
followed by grit- or shot-blasting. Degreasing by means of aqueous alkaline
solutions followed by acid etching can also be used; special treatments for
specific metals are usually laid down by suppliers of the adhesives where they
are considered advisable.[79]

In some instances, however, it may be necessary to bond rubbers after
they have been vulcanised. This method of bonding is referred to as post-
vulcanisation bonding and a main advantage is that complicated rubber shapes
may be bonded by technique which would not be technically or economically
possible by the bonding/vulcanising one-step method. For post-vulcanisation
bonding one- or two-component primer/adhesive systems are commercially avail-
able. Wake[80] has suggested that, if the bond has only to bear a light load,
cleaning the cured rubber surface with solvent, thereby swelling it somewhat,
followed by application of the adhesive may be sufficient. If the bond has
really to be load-bearing then it is necessary to remove the existing surface

of the vulcanised rubber by abrasion immediately before applying the adhesive to be used. The effects of different surface treatments for the vulcanisate prior to bonding has recently been considered by Spearman and Hutchison[81] and some of their results are given in Table 9.

Natural rubber is sensitive to the type of surface treatment, with abrasion being the most effective. Neoprene is relatively insensitive. For all three rubbers abrasion is a good pretreatment and results in high joint strengths and cohesive failure of the rubber in the joint. However, other cured rubbers such as butyl and ethylene-propylene-diene rubber are far more difficult to bond than the above, more polar natural, sbr and neoprene materials.

TABLE 9

Butt Joint Strengths (MPa) of Rubber/Metal Bonds for
Various Vulcanised Rubbers and Surface Treatments

Vulcanised rubber \ Surface treatment	Solvent wipe	Ultrasonic degreasing	Hot alkaline rinse	Abrasion	Chlorination	Cyclisation
Natural	4.5	5.4	6.5	9.4	5.6	7.0
Styrene-butadiene	1.8	6.1	6.2	7.9	6.9	4.5
Neoprene	5.1	4.9	6.7	6.8	6.9	7.0

Note: Proprietary one-coat adhesive on treated, cured rubber and two-coat primer/adhesive on metal.

7   IRRADIATION TECHNIQUES

Irradiation techniques are used on a number of substrates, and are here dealt with together for convenience. These methods include corona discharge in air and oxygen, irradiation with ultraviolet and gamma radiation and electrodeless glow discharges using a wide variety of gases.

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Corona discharge is a long established method for treating polyethylene
and is rapid and effective.[47,82] The polyethylene surface is exposed to the
corona discharge in air, usually, at atmospheric pressure. Employing infra-
red spectroscopy Rossman[83] showed that this treatment causes the formation of
unsaturated (C = C) bonds and carbonyl ($>$C = 0) groups and ascribed the
improved bonding properties to the increased surface free energy of the
polymer's surface (Figure 10). It has also been demonstrated that corona
discharge results in considerable roughening of the polymer's surface[48,84] and
at high magnification discrete bumps may be discerned on the surface. These
bumps may arise by the migration of low molecular-weight degradation products
to charged areas of the surface.

Kim, Evans and Goring[49] have studied the corona-induced autohesion of
polyethylene film. They observed that when a low-density polyethylene sheet
was treated in a corona discharge and subsequently pressed on to a similarly
treated sheet at 45°C the bond formed between them was much stronger than that
between similarly pressed, but untreated, sheets. Their studies suggested
that effects such as surface oxidation, crosslinking and rugosity were not
responsible but they proposed that the mechanism involved some type of
electret formation induced in the polymer sheet by the corona discharge.
Electrets are long-lived electrical charges induced when dielectric materials
are subjected to strong dc fields. Although 60 Hz ac was used by these
workers they claimed that charge effects produced by one cycle are not
completely neutralised by the subsequent cycle and a discrete charge is built
up on the surface by application of an ac field. They demonstrated that a
charge pattern did exist on the corona-treated polyethylene surface by
spreading a light dielectric powder on the surface of the polymer and observing
a clear "Lichtenburg figure" pattern. An important feature of this work is
that the surface charge due to electret formation is known to decay slowly with
time and, indeed, they found the autohesion of the treated polyethylene decayed
as the time between treating and bonding was increased, as is shown in
Figure 11.

This mechanism is, however, considered to be vague and physically
unacceptable by Owens.[14] His work showed that the adhesion is completely
destroyed by the application of hydrogen-bonding liquids to the adhesive joint

and the effects of such liquids is completely reversible;   joints allowed to dry regain their full, original strength.   He proposed that the corona treatment formed keto groups on the polyethylene chain;   these groups enolize and the enolic hydrogens bond with carbonyl groups in the adjacent sheet of film when the two sheets are heated together under pressure.   Owens[15] extended this work to the autohesion of polyethylene terephthalate films and showed that self-adhesion in these corona treated films was again due to hydrogen bonding but, in this instance, between carboxyl carbonyl groups in one film with phenolic hydrogens in the other.   The phenol groups were created by the corona treatment through a free radical mechanism.   Polyethylene terephthalate film could also be made self-adherent by irradiation with ultraviolet light via the same mechanism.

In 1966 Schonhorn and Hansen[85] reported a highly effective treatment for the surface preparation of low surface energy polymers for adhesive bonding. Essentially the technique consisted of exposing the polymer surface to an inert gas plasma at reduced pressure generated by electrodeless glow discharge (ie radio-frequency field).   For polyethylene only very short treatment times were necessary (Figure 12) while longer contact times were required for other polymers such as ptfe.   In subsequent work, by Hall et al[86,87] the joint strength of many polymers has been examined as a function of length of exposure to excited helium or oxygen.   Polymers examined included low- and high-density polyethylene, poly(4-methyl-1-pentene), polyvinyl fluoride, polyvinylidene fluoride, fluorinated ethylene-propylene copolymer, polyacetals, nylon 6, nylon 6.6, polyethylene terephthalate and polystyrene.   Generally, the joint strength increased rapidly initially and then remained nearly constant, perhaps decreasing in some cases at long exposure times.   Further work has dealt with the effect of gas employed,[52,88,89] gas pressure,[52] electrode separation[52] and discharge current.[52,89]

Now Schonhorn and co-workers[51,85] reported that this treatment did not change the wettability of the polyethylene, as measured by the critical surface tension, but gel permeation chromatography showed that some highly crosslinked polymer was formed after treatment and the average molecular weights, M_w and M_n, increased from 86 000 to 135 000 and 1800 to 4800 respectively.   Also, atr infra-red spectroscopy showed only the formation of transethylenic unsaturation

after treatment and a thin intractable skin was readily observed by melting the polymer. Schonhorn concluded that wettability was not the sole criterion for the formation of an adhesive joint but what may be of greater importance is to enhance the cohesive strength of a weak surface region. He suggested that many melt crystallised polymers possess an inherent weak boundary layer, about 0.02 to 0.10 µm thick, which is composed of amorphous low molecular-weight materials rejected by the crystallisation process which starts in the bulk and proceeds outwards. It was therefore concluded that the increases in joint strength achieved by this technique were primarily due to increasing the cohesive strength of the polymer in the surface regions by the introduction of crosslinks. The surface treatment was therefore called CASING (Crosslinking by Activated Species of Inert Gases).

A major criticism of Schonhorn's proposal that a weak amorphous surface is produced when polymeric films are melt crystallised in air is that his evidence is mainly inferred. Indeed, recent work by Briggs and co-workers[64] using XPS found no evidence of joint failure occurring in the surface regions of the polyethylene substrate. Further, several workers[37,52,53,90,91] have established that the surface free energy of the polymer may be increased by glow discharge treatment; thus surface energetics, surface roughening and the production of chemically active surfaces, to which grafting may occur, may account for the observed increased adhesion.

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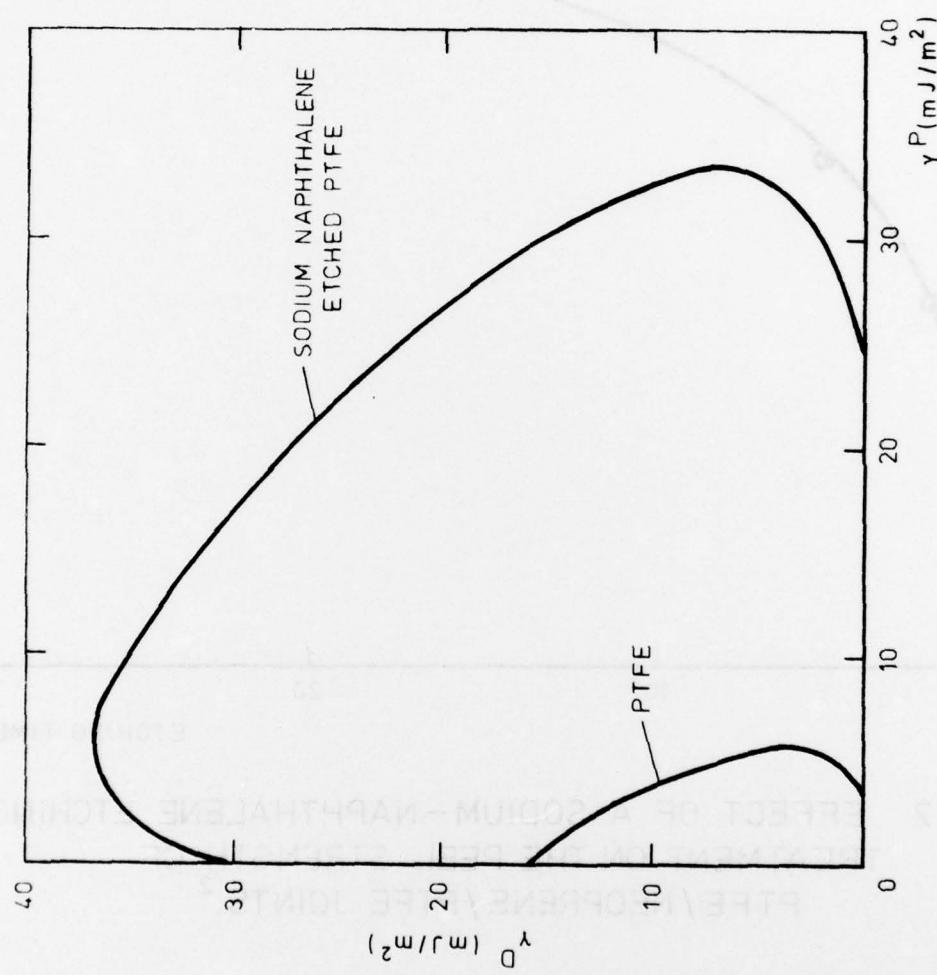
FIG. 1 WETTABILITY ENVELOPES OF PTFE AND ETCHED PTFE.[12]
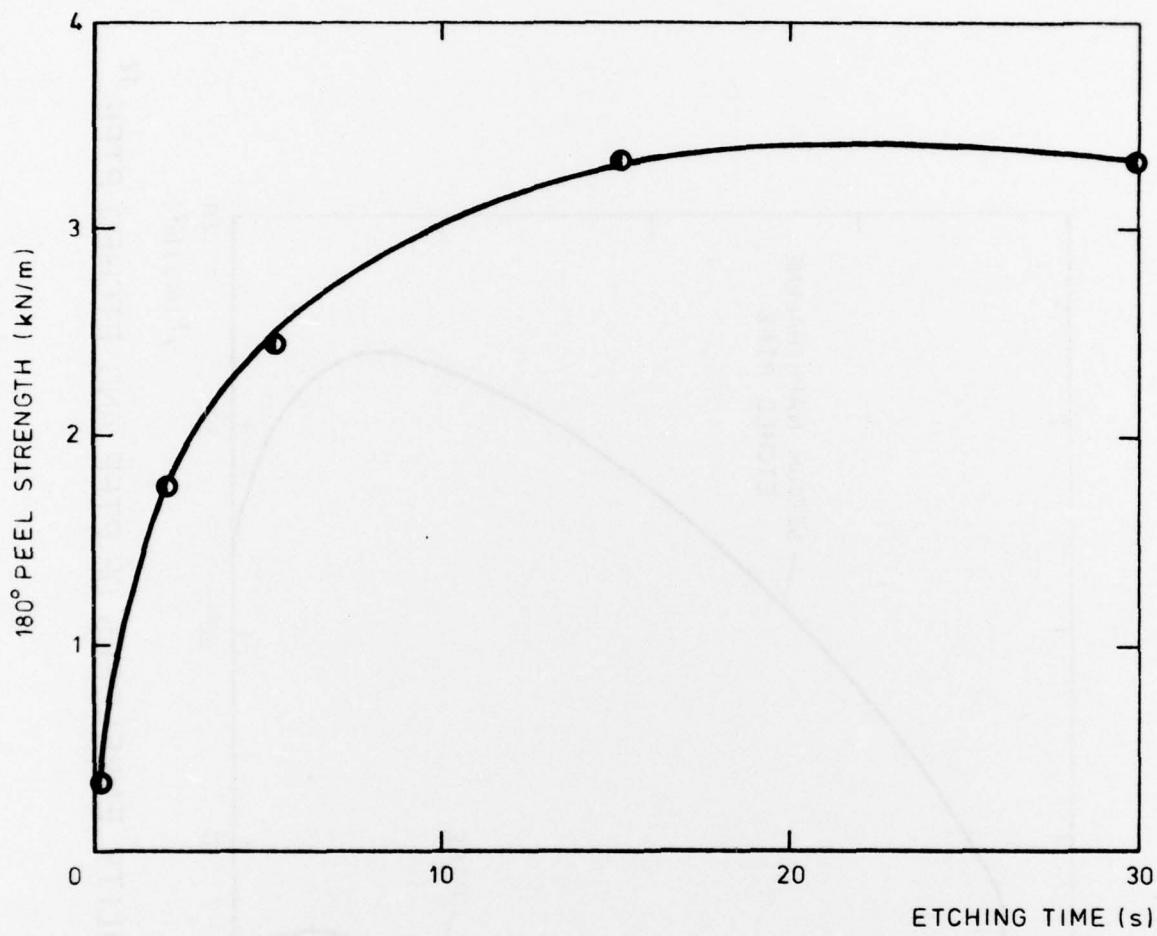
FIG. 2   EFFECT OF A SODIUM–NAPHTHALENE ETCHING
TREATMENT ON THE PEEL STRENGTH OF
PTFE / NEOPRENE / PTFE JOINTS.[2]
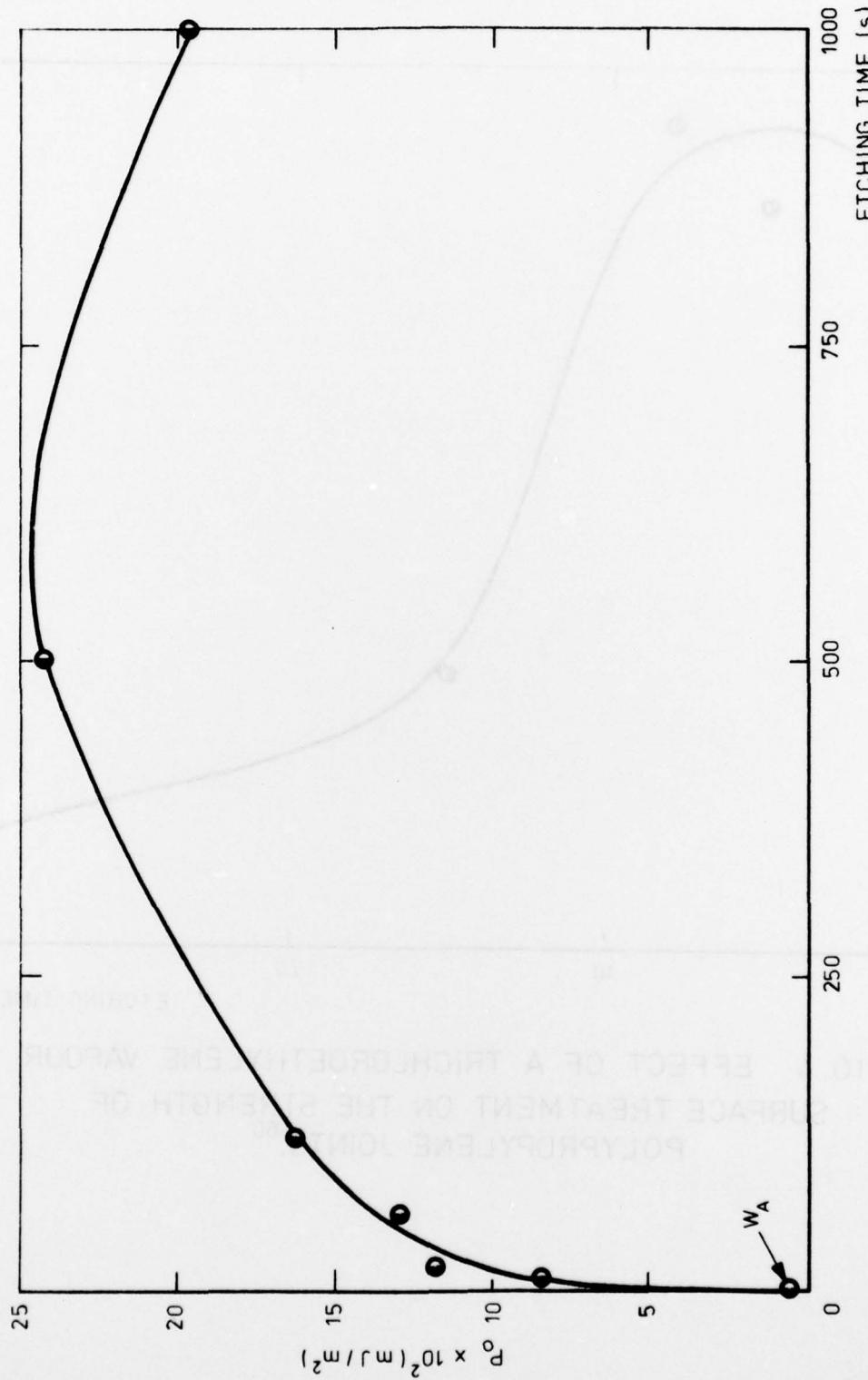
FIG. 3 INTRINSIC ADHESIVE FAILURE ENERGY, P_O, VS ETCHING TIME FOR RUBBER / FEP JOINTS.[37,39]
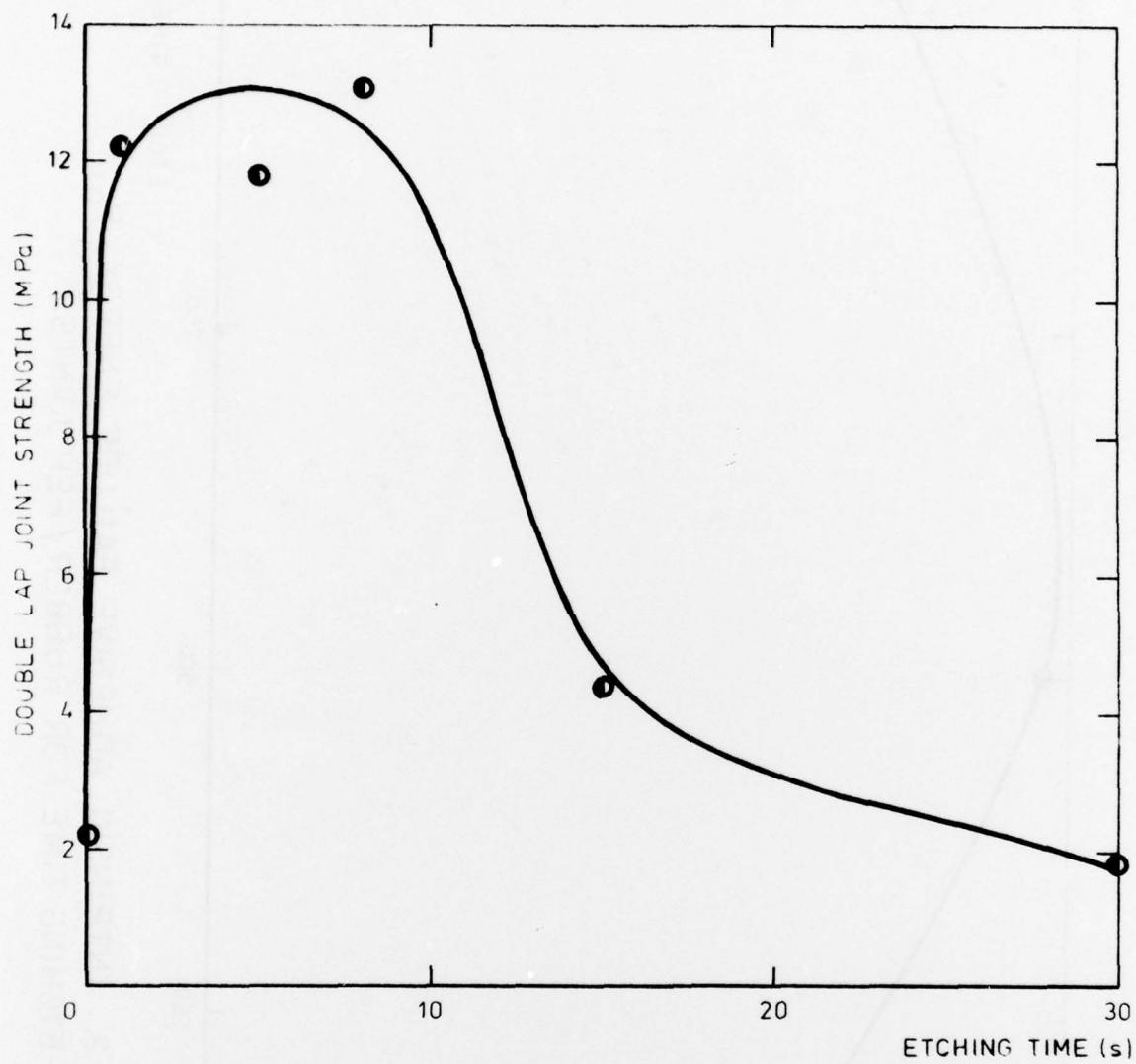
FIG. 4   EFFECT OF A TRICHLOROETHYLENE VAPOUR
SURFACE TREATMENT ON THE STRENGTH OF
POLYPROPYLENE JOINTS.[60]
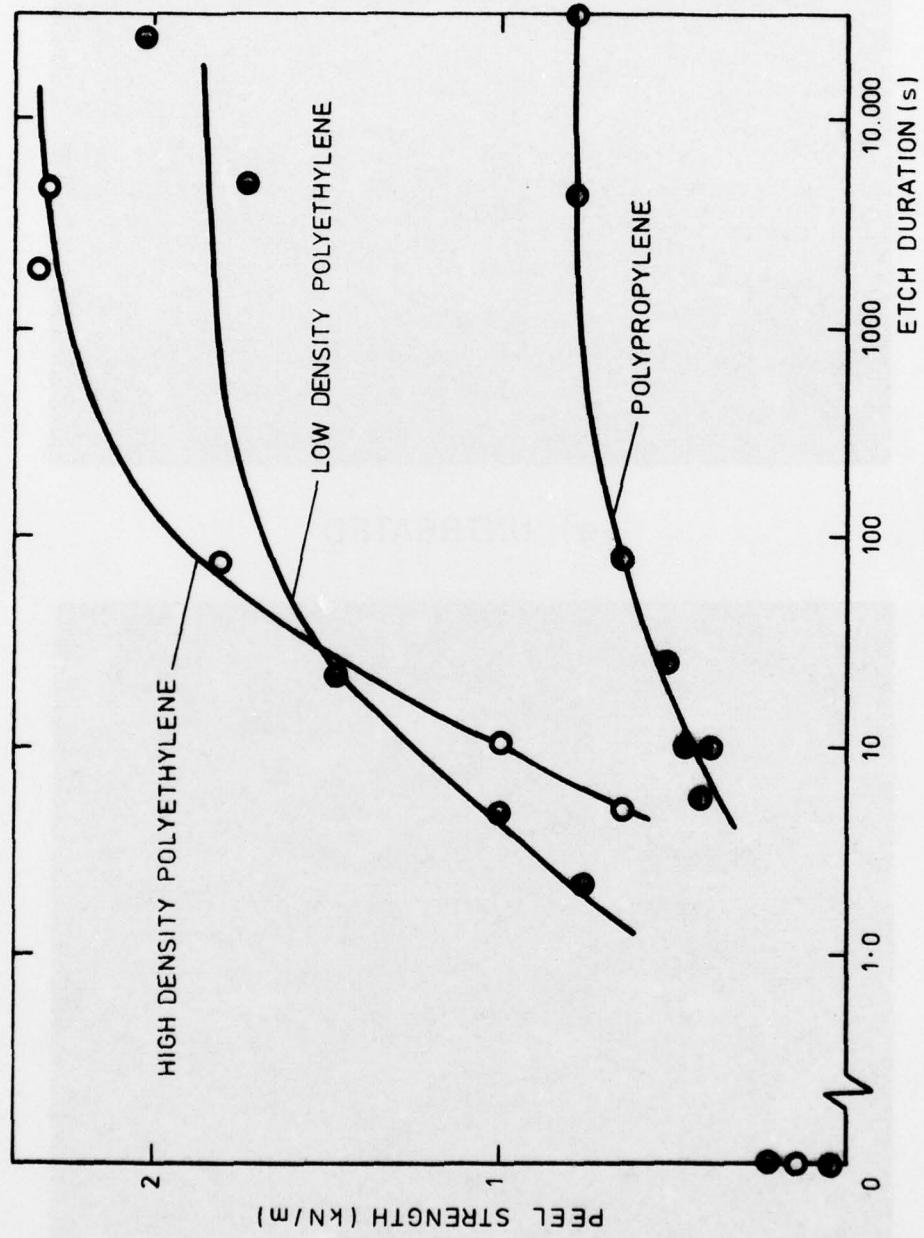
FIG. 5 PEEL STRENGTHS FOR ETCHED POLYOLEFIN SURFACES
AS A FUNCTION OF ETCH TIME
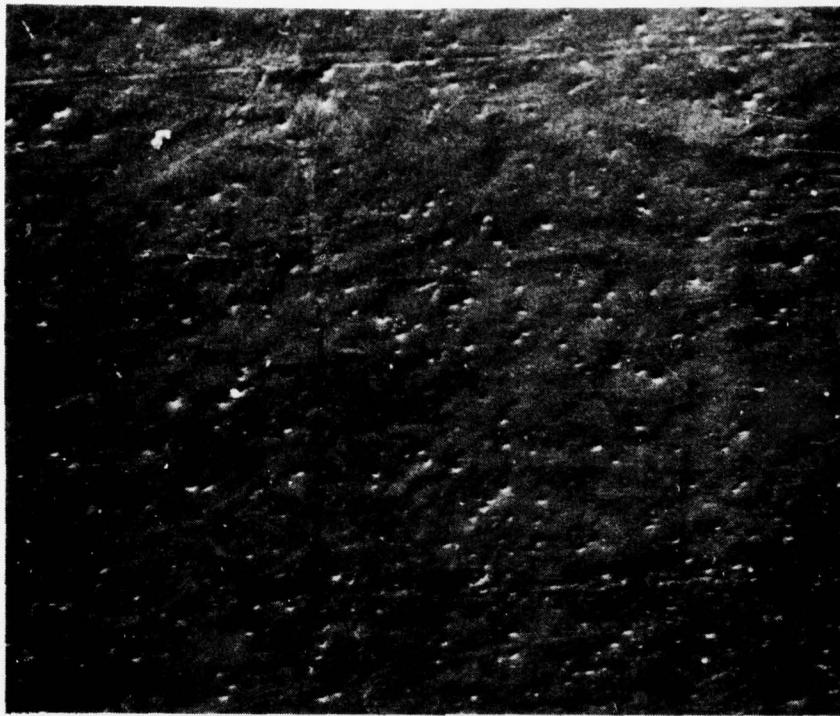
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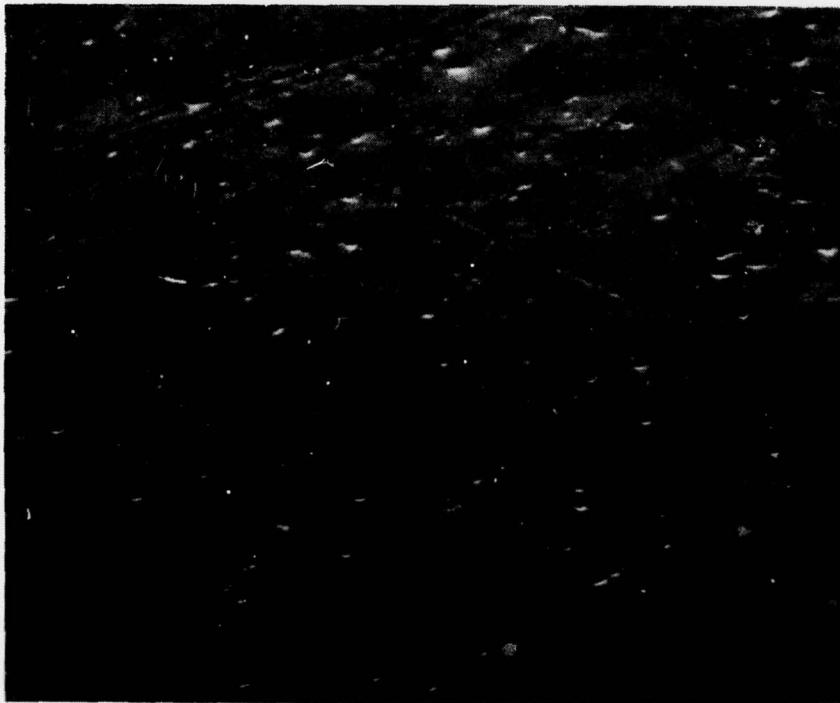
(b) ETCHED FOR 10 MIN AT 20°C

FIG. 6   SURFACE TREATMENT OF POLYPROPYLENE WITH CHROMIC ACID;
EFFECT OF VARIATION IN TIME AND TEMPERATURE. [2]
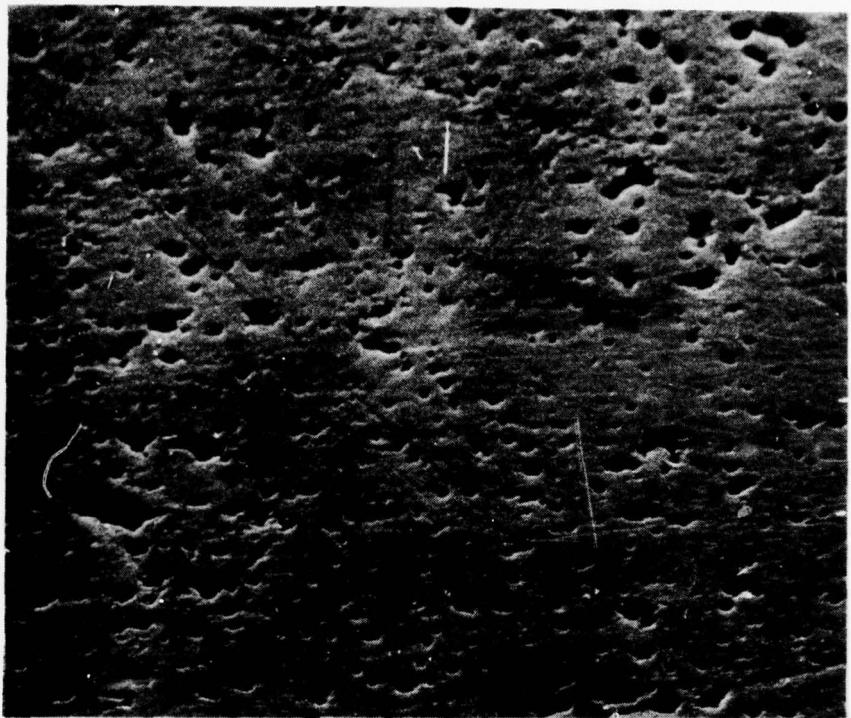
(c) ETCHED FOR 20 MIN AT 20°C
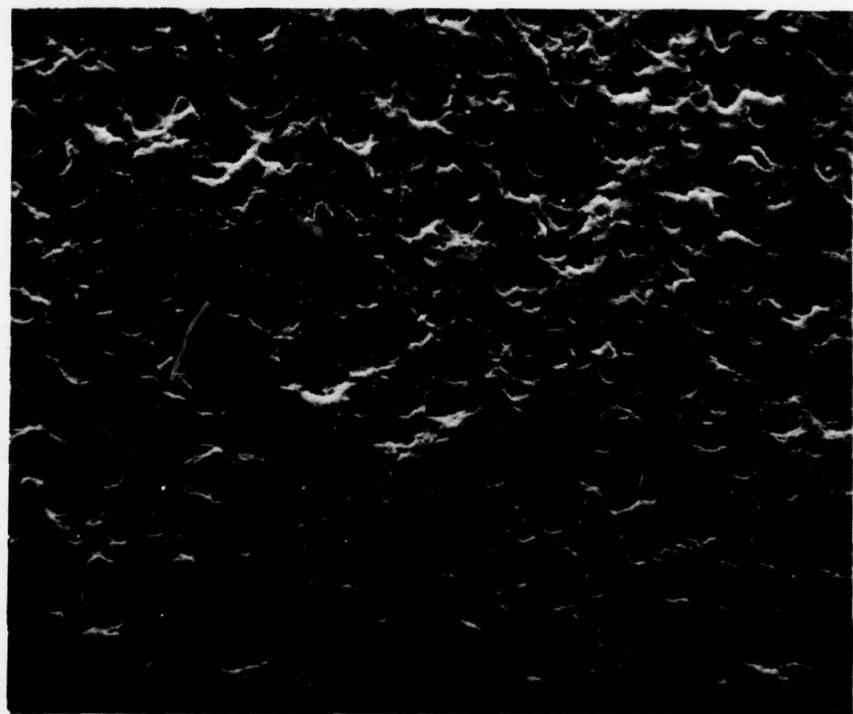
(d) ETCHED FOR 5 MIN AT 80°C

FIG. 6
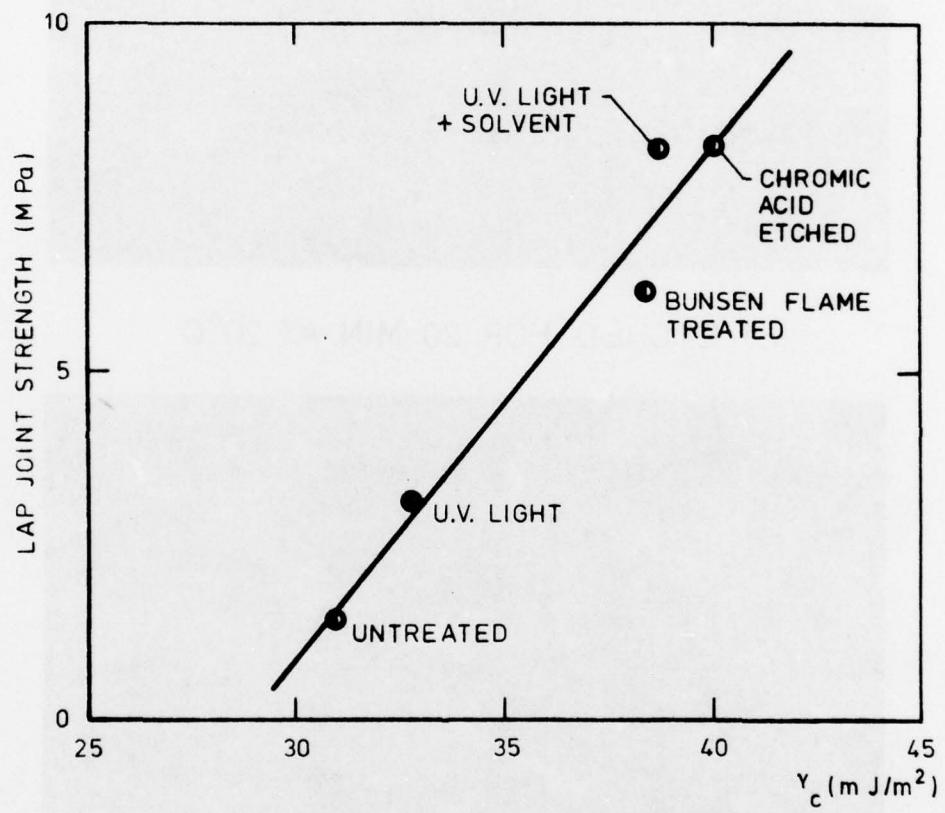
FIG. 7   LAP JOINT STRENGTH VS CRITICAL
SURFACE TENSION FOR POLYETHYLENE
TREATED BY VARIOUS METHODS
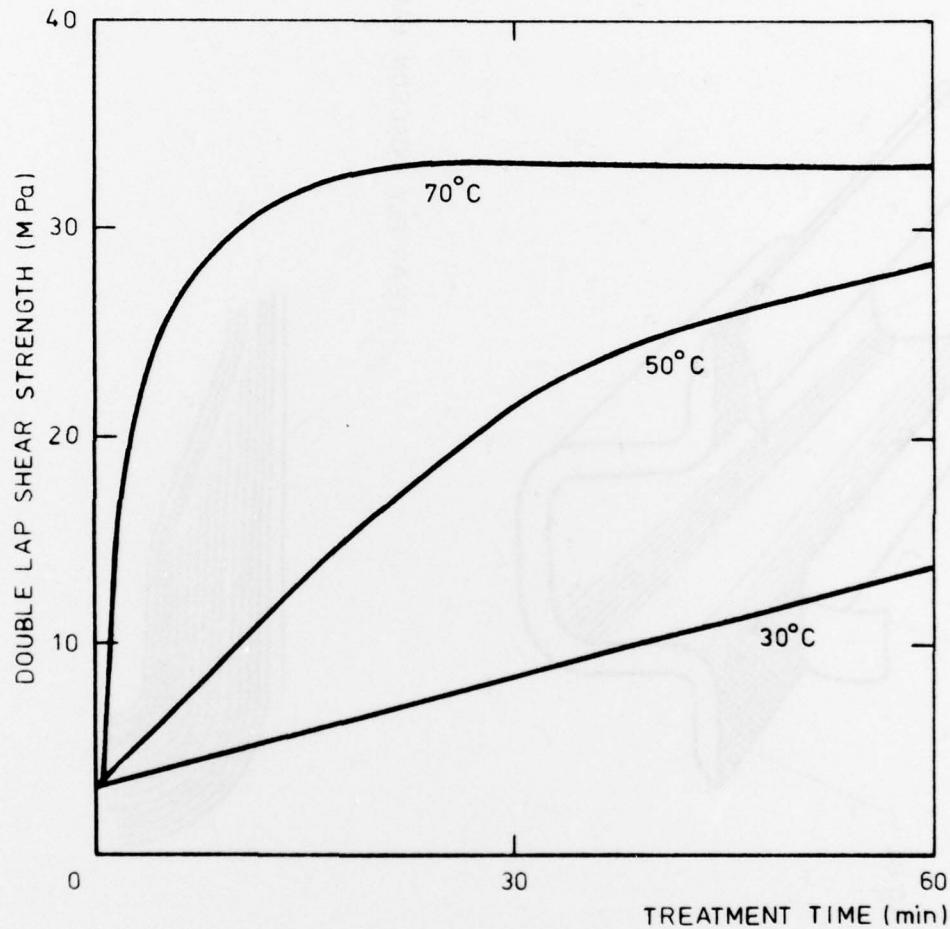
FIG. 8   EFFECT OF TREATMENT TIME AND TEMPERATURE
ON ADHESIVE JOINT STRENGTH OF POLYETHYLENE
TREATED WITH 0·26 M SOLUTION OF $(NH_4)_2 S_2 O_8$

TEAR PLY

TEAR PLY

SURFACE TO BE
BONDED

TEAR PLY (DACRON FABRIC)
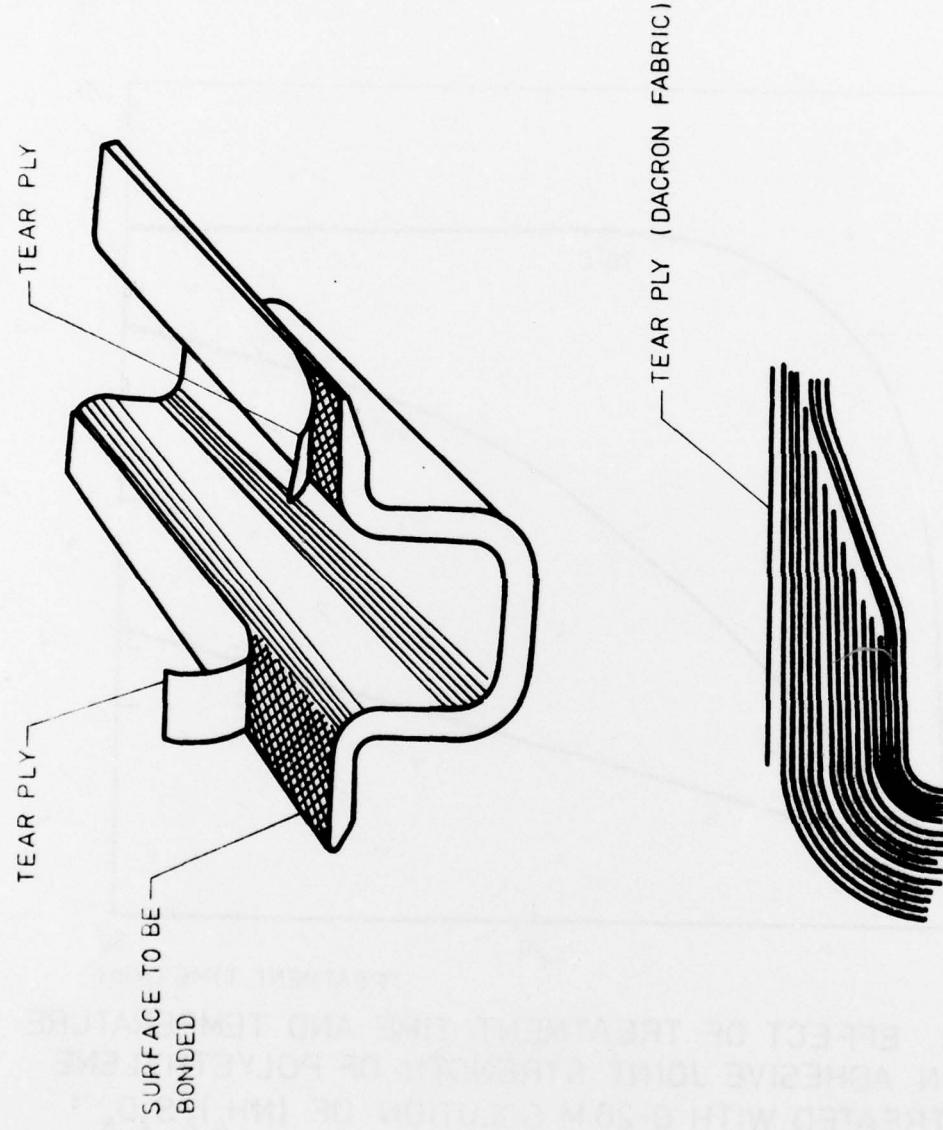
FIG. 9   STRUCTURAL REINFORCED PLASTIC LAMINATE WITH TEAR PLY
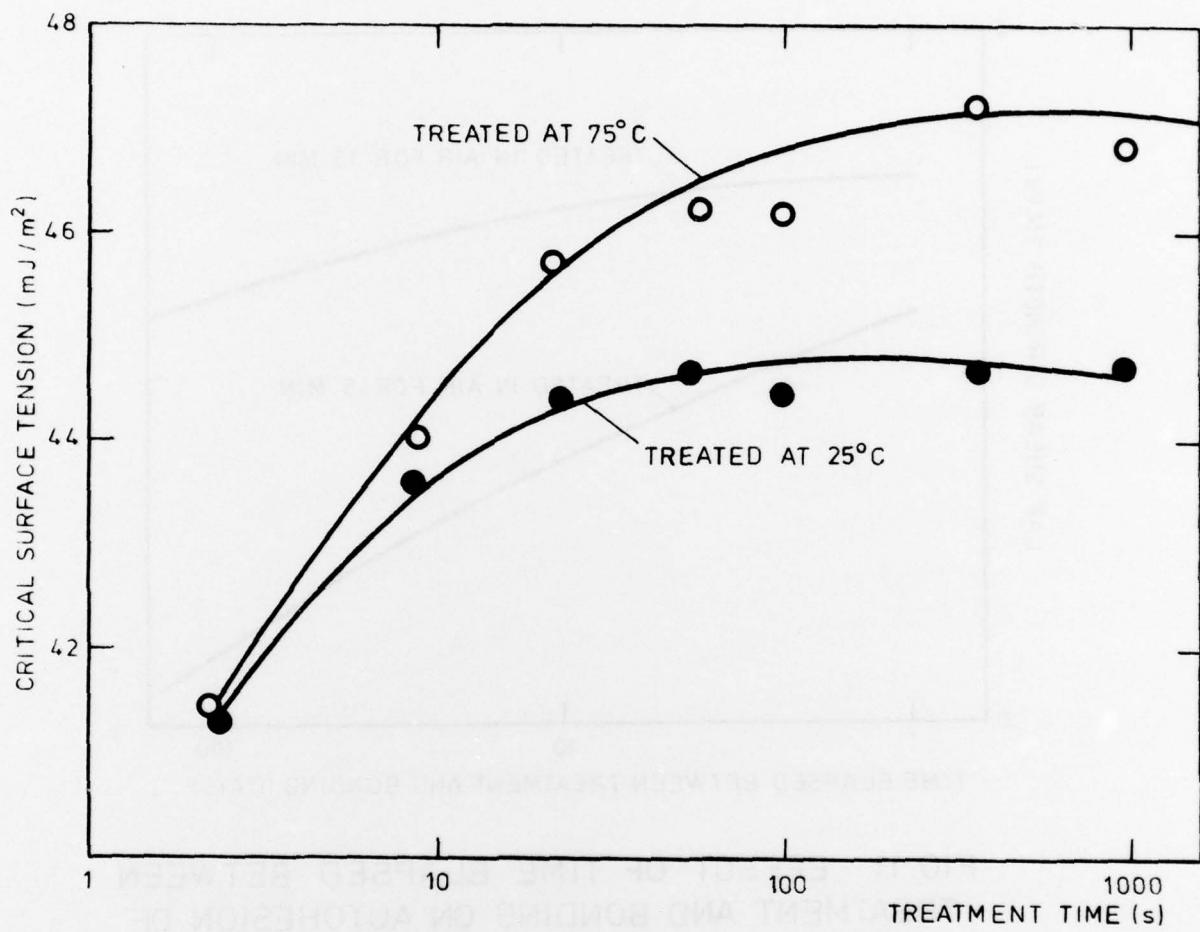
FIG.10   CRITICAL SURFACE TENSION VS TIME OF TREATMENT
FOR POLYETHYLENE TREATED IN AIR CORONA
AT DIFFERENT TEMPERATURES.[49]
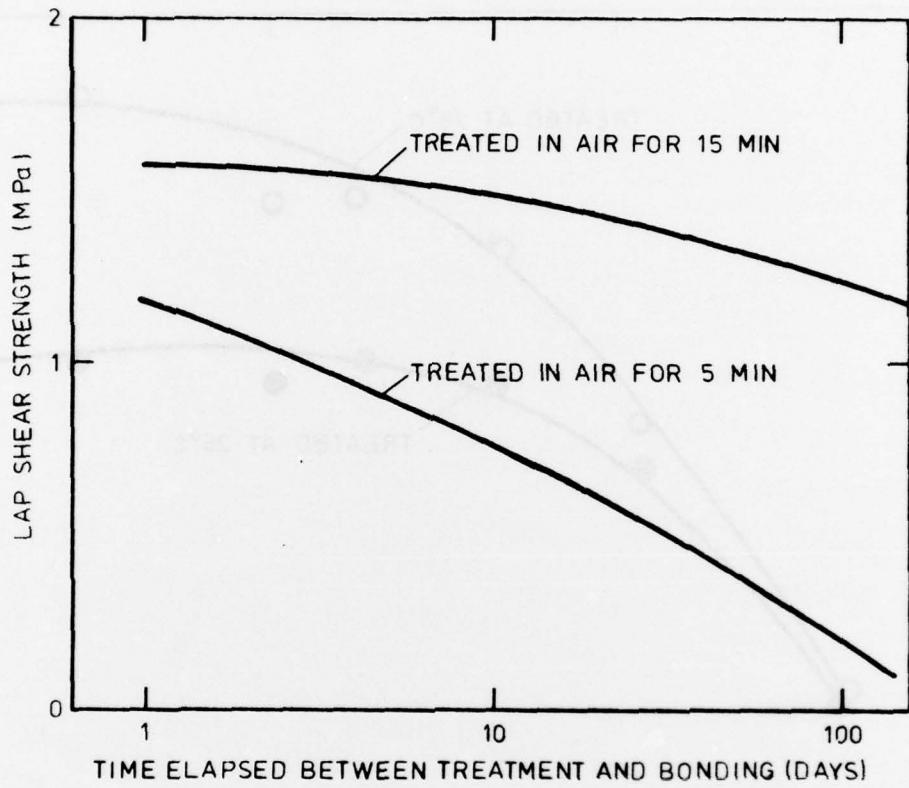
FIG. 11   EFFECT OF TIME ELAPSED BETWEEN
TREATMENT AND BONDING ON AUTOHESION OF
CORONA-TREATED POLYETHYLENE.[49]
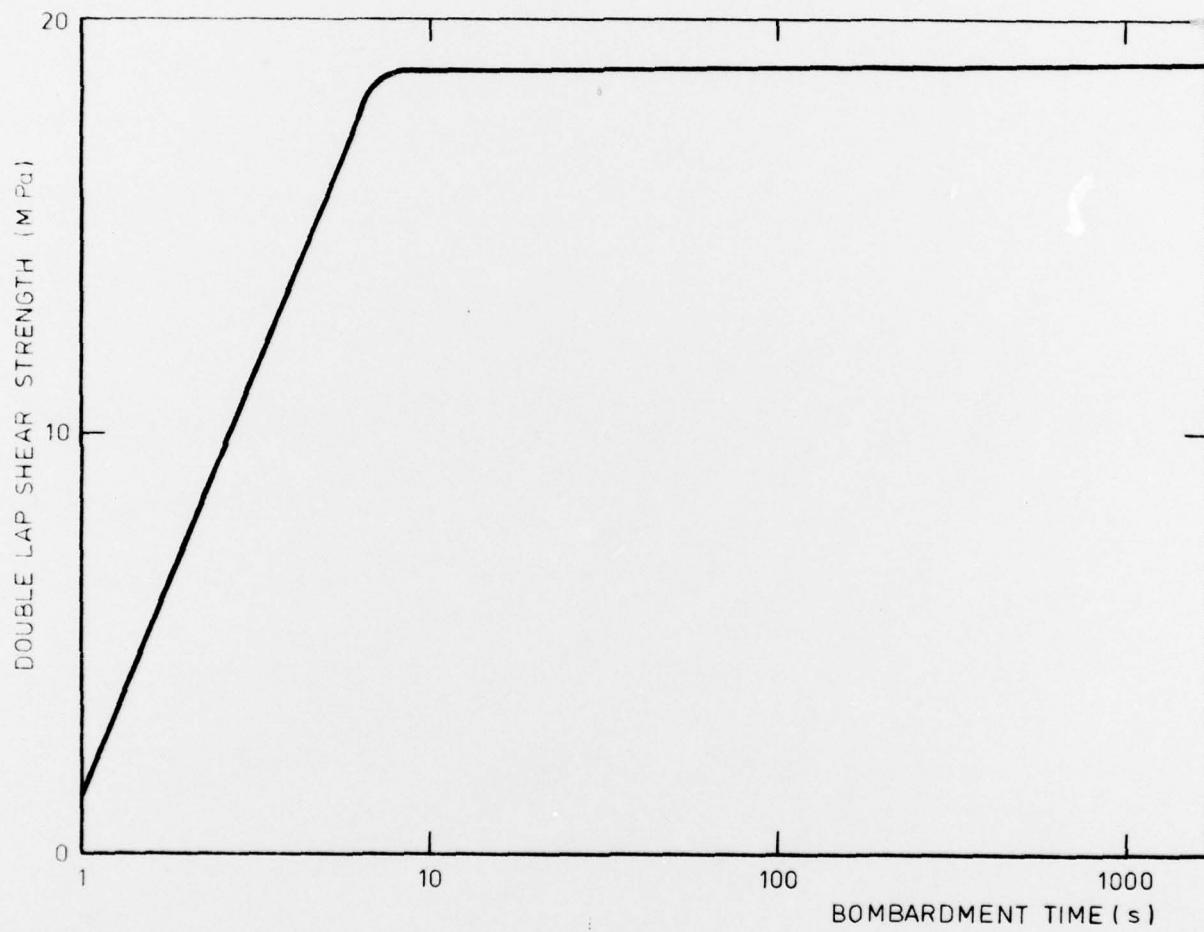
FIG.12   LAP SHEAR STENGTH OF ALUMINIUM/EPOXIDE/TREATED
POLYETHYLENE JOINTS AS A FUNCTION OF
BOMBARDMENT TIME IN HELIUM PLASMA.[50]

REPORT DOCUMENTATION PAGE

(Notes on completion overleaf)

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5. Originator's Code (if known) 445050	6. Originator (Corporate Author) Name and Location Propellants, Explosives and Rocket Motor Establishment Waltham Abbey Essex England		
5a.Sponsoring Agency's Code (if known)	6a.Sponsoring Agency (Contract Authority) Name and Location		

7. Title

PREPARING LOW-ENERGY SURFACES FOR BONDING

7a.Title in Foreign Language (in the case of translations)

7b.Presented at (for conference papers).Title, place and date of conference

8. Author 1.Surname, initials Dukes W A	9a Author 2 Kinloch A J	9b Authors 3, 4...	10. Date 1.1978	pp 42	ref 91
11. Contract Number	12. Period	13. Project	14. Other References		

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Descriptors (or keywords)

Surfaces, Surface energy, Surface finishing, Adhesive bonding, Chemical etching,
Abrasion, Cleaning, Solvents, Fluorohydrocarbons, Polymers, Plastics, Olefin
resins, Polyamide resins, Fiber laminates, Elastomers, Irradiation

(TEST)

Abstract

Techniques for preparing low-energy surfaces prior to adhesive bonding
are reviewed, and the mechanisms whereby the various treatments work are
discussed in detail.